

## Complexometric Titration

### **Titration:**

Titration is a method in which we use the solution of known concentration to determine the concentration unknown solutions.

### **Complexometric titration**

A complexometric titration is type of volumetric titration which is based upon the formation of coordination complex. Complexometric titration is mainly used for the determination. Different metal ions in solution. Simple ion transformed in to complex ion and the equivalence point is determined by using

### **Complex:**

A complex can form only when the central atom which is the middle ion accept an electron pair from or more ligand.

### **Principle of Complexometric Titration:**

In complexometric titration the indicator that we use are known as colorimetric dyes so this indicator binds with metal ion and form colored complexes so when we add the chelating agent in the middle indicator complex solution this chelating agent it replaces the middle from the middle indicator complex since chelating agent always bind much more strongly with the middle cation then the indicator that's why it replaces the indicator from the middle indicator complex and itself bind with the metal to form the metal complex now the indicator free from middle indicator complex as the titration goes on at the end of titration all the indicator get replaced by

the chelating agent and then it shows the color change of the solution and change the color of the solution determine the point of our titration

### Complexometric reagents:

There are following most important reagent.

1. EDTA (Ethylene Diamine tetra acetic )
2. DTPA (Diethylene triamine penta acetic acid )
3. EGTA
4. Ammonia
5. Ethylene Diamine

### Advantage of complexometric titration:

- Accurate and fast
- Difficulty due to formation of stepwise complex can be minimized for almost all the metal ions coordination number is either 4 or 6. With monodentate ligands multi step reactions are required so at one time number of complexes are present in a reaction mixture making it difficult to observe sharp equilibrium point.
- To overcome these problems multidentate ligands are used. EDTA is the most commonly used ligand. EDTA has 6 coordination sites (4 O and 2 N) and forms 1 : 1 strong metal complex.

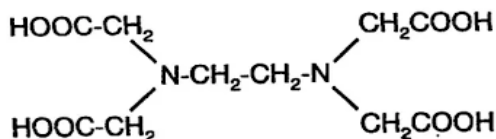


Figure:1 structure of EDTA

Disodium salt of EDTA is generally used for titrations.

- The formation constant for various metal ions with EDTA are given below. The data indicates that except for group I metal ions ligand combines with almost all the metal ions. The lower stability of M-EDTA complex and high pH of solution must be maintained during titration.

### Types of EDTA titrations:

- **Direct titrations:** These titrations involve titration of metal ion with ligand directly. Some auxiliary ligand such as amoni, titrate and citrate etc be employed to prevent metal hydroide formatio.
- **Back titrations:** Under certain circumstances the direct titration are not feasible. These condition include:
  - Precipitation of metal in necessary pH range required for titration.
  - Slow reaction between metal and ligand.
  - Unavailability of suitable indicator.
- **Substitution titrations:** these titraion is suitable where end point is not sharp or metal indicator complex is not formed. These titration are also suitable where metal EDTA complex is more stable than Mg-EDTA complex.
- **Alkalimetric titrations:** these titraion are based on principle redox titraton with liberated hydrogen from the reaction of heavy metal ion with sodium salt of EDTA. The titraion is carried out without any buffer with base like NaOH.

### End point Detection:

- Metallochromic indicators are used for end point detection.
- Colored organic compound from complexes with metal ions
- Stability of M-EDTA complexes should be higher than M – ind complexes
- Erichrome Black T (EBT)
- EBT is useful for titration in pH range 7-10 which includes complexation of calcium, magnesium and zinc.
- EBT is triprotic and has a different structure at varying pH values
- Between pH 7 and 10 it exist as the di anion and is blue in color again forms red color complexes with metal ion.

### **EDTA Titrations: Selectivity:**

Wide variety of metal ions form complexes with EDTA. So for determination of particular metal in presence of other interferences, masking agents are added to bind interferences. After the initial titration releasing agents are added to proceed in forward direction. Following methods are used for masking

- **Precipitation:** During the titration of hard water coprecipitation of calcium and magnesium can be avoided if magnesium ions are precipitated as hydroxides at pH 12 and calcium alone can be detected in the initial reaction
- **Oxidation state:** titration metals ion exist in variable oxidation state. The stability constant for one oxidation state may differ from other oxidation state. As in case of Fe(3) forms stable complex with EDTA than Fe(II).
- **pH:** For the following reaction, as they acidity increases the equilibrium of reaction shifts toward left direction. So the high pH is maintained throughout the reaction using a buffer solution. The calcium and magnesium ions

are determined at high pH, however low pH is maintained for the determination of Fe(III).

Determination the Amount of Calcium and Magnesium present Hard Water

- **Hardness of water:** It's measured in terms of calcium and magnesium ions present in water. It may temporary if carbonates and bicarbonates of calcium and magnesium are there in water and permanent if chlorides or sulphates of calcium and magnesium are there. Temporary hardness can be removed by boiling the water where as permanent hardness can ne removed by ion exchange method.
- **Analysis of the water:** pipette out 25 ml of the sample solution into titration flask, add 4ml of pH 10 buffer, 2 drops of Eriochrome Black T indicator.Heat the solution to about 60<sup>0</sup>C and titrate with EDTA solution until a purple color is obtained. Shake the solution then continue titrating, adding EDTA drop wise with constant shaking until blue color with tinge of purple is obtained. This gives total Ca (II) and Mg (III) concentration.
- **Determination of Ca (II):** pipette out 25ml of sample solution and add 3ml of 50% NaOH. The Mg (III)will precipitate as Mg (OH)<sub>2</sub>. Shake the solution vigorously. Add 2 drops of calcon indicator and titrate with EDTA drop wise until a drop of EDTA turns the solution blue, but purple color will appear within 20 seconds. Allow the solution to stand for 5 minutes with occasional stirring. Some of the calcium is precipitated as CaCO<sub>3</sub>,this allows the dissolution of CaCO<sub>3</sub> to ensure correct end point.Continue titration unless blue color persistent for 20 seconds is obtained.

### Calculation :

- 1ml 0.01 M EDTA = 0.4008 mg Ca(II)
- 1 ml 0.01 M EDTA = 0.2731 mg Mg(III)

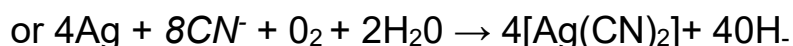
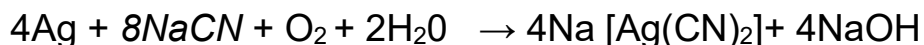
- volume of EDTA Consumed with EBT for total hardness (Ca( ) and Mg ( ) = x ml
- volume of EDTA Consumed with calcon indicator for Ca(II ) only = Y ml
- mg of Ca(II) = 0.4008 Y
- mg of Mg(II) = 0.2731 (X-Y)

## Applications of Complexes in Metallurgy

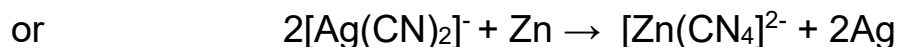
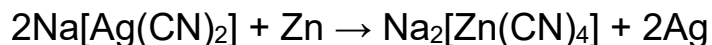
### 1. Extraction of Ag and Au by Mac-Arthur and Forest Cyanide

#### Process

(i) Ag is extracted from argentite ore (Ag<sub>2</sub>S) by cyanide process. The concentrated Ag<sub>2</sub>S ore is treated with a dilute solution of NaCN (0.5%) for several hours in presence of air so that metallic Ag and AgCl present in the ore and Ag<sub>2</sub>S ore itself are converted into soluble sodium dicyanoargentate (I), Na[Ag(CN)<sub>2</sub>].



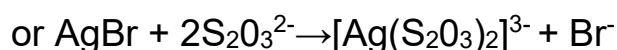
Now Ag is precipitated out from Na[Ag(CN)<sub>2</sub>] by more electropositive Zn metal. Being more electropositive, Zn displaces less electropositive Ag metal from Na[Ag(CN)<sub>2</sub>]



(ii) We know that the tailings obtained from amalgamation process and the auriferous quartz rocks contain gold. Cyanide process can be used to get gold metal from these tailings and auriferous quartz rocks. In this process the tailings or rocks are treated with KCN solution in presence of atmospheric  $O_2$  when Au present in tailings or rocks is converted into soluble pot. dicyanoaurate (I),  $K[Au(CN)_4]$  (complex compound) from which Au can be precipitated by adding Zn.

### 3. In Photography

In photography, when the developed film is washed with hypo solution (i.e. solution of sod. thiosulphate,  $Na_2S_2O_3$ ), the negative film gets fixed (i.e. the image becomes permanent). In the fixing process the unrecompensed AgBr (i.e. AgBr which has not decomposed to Ag in the process of developing) gets dissolved in  $Na_2S_2O_3$  solution as a soluble complex,  $Na_3[Ag(S_2O_3)_2]$  which is called sod. dithioorgenate (I).



$Na_3[Ag(S_2O_3)_2]$  formed above is colourless and soluble in water and hence can be easily removed by washing the photographic plate or film with water.

### 4. As dyes or Pigments

Phthalocyanine blue which is extremely stable complex of copper (II) is one of the many complex compounds used as dyes or pigments.

### 5. Softening of Hard Water

We know that hard water contains  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  salts dissolved in it. Soap gives precipitate of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  salt with hard water and thus more quantity of soap is used in washing the clothes. In order to prevent the formation of the precipitate of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  salt, we use excess of polyphosphates and polydentate amino acids as sequestering agents. These complexing agents form *water-soluble* complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in hard water and thus the precipitation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  salt with hard water is prevented and hard water becomes soft. Ethylenediamine tetra acetic acid ( $\text{EDTAH}_4$ ) has also been used for softening hard water which does a lot of harm in industrial boilers and other equipments by forming a scale in them. Ethylenediamine tetracetic acid is added to the boilers etc. in which  $\text{EDTA}^{4-}$  forms water-soluble complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in hard water and thus these ions are removed.

Ion-exchange resins have also been used to remove both cations and anions from aqueous solution and deionized water so obtained equivalent to distilled water in purity.

## 6. Food Preservation

Freshly fruits, fruit juice, green vegetables containing vitamin C, on keeping for sometime get spoiled since even one part per million parts of metal ions catalysis. Atmospheric oxidation which spoils these eatables. The addition of one hundredth 1% of a masking agent like ethylenediamine tetra acetic acid improves the quality the food on standing by catching the traces of metals by chelate formation.

## Application of Complexes in Medical Field



Many complex compounds are used as medicines for the treatment of various diseases. For example,

(i) Ca-EDTA chelate,  $\text{Ca}[\text{EDTANa}_2]$  is used in the treatment of lead poisoning (i.e., for removing lead from the body).

(ii) *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  (called cisplatin) is used as an antitumor agent in the treatment of cancer. *cis*- $[\text{Pt}_2+(\text{NH}_3)_2\text{Cl}_2]\text{O}$  has square planar geometry.

(iii) Lewisite,  $\text{ClCH}=\text{CRAs} / \text{Cl}$  is an arsenic compound and is a deadly poisonous gas. This gas was used for mass killing during the first world war. 2, 3-dimercapto propanol which is named as British Anti Lewisite (BAL) was used as antidote. 3-dimercapto propanol forms a complex with Lewisite and thus destroys the poisonous effect of Lewisite.

(iv) Metals present in toxic proportions in animals and plants are removed by *chelate therapy*, e.g., excess of copper and iron are removed by using chelating ligands, D-penicillamine and desferioxime-B.

(5) Sodium salt of 2, 3-dimercapto propane-1- sulphonic acid has been used for treating the poisoning caused by metal ions like Bi, Hg, Cu, Au, etc. These metal ions are strongly bound by the chelating ligand. Presence of metal complexes in Biological systems

Biological systems contain a number of metal complexes. These complexes make the metal available to the biological systems which may not be otherwise easily available. A few examples of biological metal complexes are given below.

## 1. Hemoglobin

Blood contains red blood corpuscles (RBCs). About 95% of RBCs is composed of hemoglobin. Hemo group is an important part of hemoglobin. Therefore, before discussing the structure of hemoglobin, we should discuss the structure of heme group. Heme group is a complex compound of Fe (II) with tetra dentate macro cyclic ligand namely porphyrin. In heme group Fe (II) is attached with all the four N-atoms of porphyrin ligand. All the C-atoms of the ring system, coordinating N-atoms and the central Fe (II) lie in the same square plane.

Haemoglobin is a HS octahedral complex of Fe (II). Fe(II) has four unpaired electrons [ $\text{Fe}^{2+} = 3d^6 = t_{2g}^4 e_g^2 (n = 4)$ ]. The centre of the octahedral structure is occupied by Fe (II) which is attached with four N-atoms of the heme group placed at the four corners of the C square plane. Fe (II) is also attached with N-atom present in protein placed at one axial position and with  $\text{H}_2\text{O}$  molecule placed at the other axial position. The function of hemoglobin in our body is to supply  $\text{O}_2$  to various parts of body. Thus hemoglobin produces energy which is utilized by living organisms to perform their various metabolic activities.

## 2. Chlorophyll

Chlorophyll is a green-coloured matter (pigment) present in green plants and algae. It contains the basic unit, porphyrin ring. It is a square planar complex containing  $\text{Mg}^{2+}$ . Thus it is a naturally occurring chelated complex of Mg. The Mg- atom in chlorophyll lies slightly above the plane of the rigid chelate ring structure. The chlorophyll molecule can add to it one or two water molecules axially. Such coordinated water molecules then help in associating other chlorophyll molecules through hydrogen bonding.

There are various modifications of chlorophyll. All these modifications contain porphyrin ring and differ from each other in the side groups of the porphyrin ring. The most abundant chlorophyll is *chlorophyll a*. Chlorophyll present in plants helps in the process of photosynthesis which is in plants. In this process carbohydrates are produced in plants in presence of sun light and chlorophyll. Thus chlorophyll, acts as a photosensitizer in the synthesis of carbohydrates in plants.

**Mechanism of photosynthesis.** Photosynthesis is a process in which  $\text{CO}_2$  and moisture of the atmosphere combine together in the presence of sunlight and chlorophyll and produce glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) and  $\text{O}_2$ . Glucose is further converted to polysaccharides like starch. In a simplified way, the process of photosynthesis

### **Vitamin B12 (Cyanocobaltamine)**

Vitamin  $\text{B}_{12}$  is a complex of cobalt (I) with a tetradentate ligand which is similar to porphyrine found in hemoglobin. Vitamin  $\text{B}_{12}$  does not occur in plants but occurs in animals and microorganisms. It is found in eggs and livers of ox, sheep, pig, fish etc. It has been found in rain water where its presence is attributed to microorganisms sucked up by winds. Vitamin  $\text{B}_{12}$  is soluble in water and stable to heat. The deficiency of Vitamin  $\text{B}_{12}$  causes pernicious anemia, inflammation of tongue and mouth.